

# The effect of annealing on the proton conductivity of Mg-doped $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

Yuji Okuyama<sup>1</sup>, Noriaki Kurita<sup>2</sup>, Keiichi Katayama<sup>2</sup> and Norihiko Fukatsu<sup>2</sup>

<sup>1</sup> *Intellectual Property Division, Industry-Academia-Government Collaboration Center, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

<sup>2</sup> *Department of Materials Science and Engineering, Graduate School of Engineering, Omohi College, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

E-mail: okuyama@imono.mse.nitech.ac.jp

FAX: +81-52-735-5571

TEL: +81-52-735-5315

**Abstract.** In order to evaluate the effect of annealing treatment on the proton conductivity of  $\alpha$ -alumina, the electrical conductivity of Mg-doped polycrystalline  $\alpha$ -alumina kept at 1873 K under various conditions of the surrounding atmosphere and then cooled in the furnace was measured in the temperature range 1173-1473 K. The H<sup>+</sup>/D<sup>+</sup> isotope effect on the electrical conductivity was also examined under a hydrogen atmosphere at 1273 K. The protonic conductivity measured at 1273 K increased with the increase in the activity of oxygen and water vapor in the annealing atmosphere at 1873 K. It is considered that the solubility limit of magnesium ions in  $\alpha$ -alumina in equilibrium with the small amount of the spinel phase increased with the increase in the activity of oxygen and water vapor at 1873 K. This enhanced amount of magnesium ions is frozen in a non-equilibrium state to 1273 K and works as the enriched acceptor dopant for the incorporation of protons.

*Keywords*

proton conductors,  $\alpha$ -alumina, electrical conductivity, annealing effect

## Introduction

The electrical conductivity of  $\alpha$ -alumina has been studied by many researchers for a long time [1-7]. In many studies, however, the effect of hydrogen defect on the conductivity has been neglected. El-Aiat and Kröger suggested first the effect of the hydrogen defect on the electrical conductivity and reported that vanadium-doped  $\alpha$ -alumina shows proton conduction [8].

A single crystal of  $\alpha$ -alumina doped with a bivalent cation has proton conduction in a hydrogen atmosphere [9-13]. According to reports on the emf measurement of a gas concentration cell using commercial  $\alpha$ -alumina as a solid electrolyte,  $\alpha$ -alumina is a mixed proton and hole conductor at 1273-1673 K [14-16]. The protonic transport number of  $\alpha$ -alumina is higher than that of a perovskite-type proton conductor [17] if compared at the high temperature. Moreover, the conduction of oxide ions and aluminum ions in  $\alpha$ -alumina is negligible in the temperature range of 1073-1673 K. Therefore, this material is favorably used as the electrolyte of the emf-type hydrogen sensor for the process control of melting copper [16].

The conductivity of  $\alpha$ -alumina is significantly lower than that of the perovskite-type proton conductor [18]. It is attributed to the extremely low solubility limits of bivalent cations which work as the acceptor of the electron of the incorporated hydrogen in  $\alpha$ -alumina. It is necessary to increase the conductivity as much as possible for the effective use of  $\alpha$ -alumina as the solid electrolyte of a hydrogen sensor used over a wide temperature range.

The purpose of this study is to optimize the manufacturing conditions of sintered  $\alpha$ -alumina for use in a hydrogen sensor. In this study, the electrical conductivity of Mg-doped  $\alpha$ -alumina annealed in various conditions of the surrounding atmosphere at 1873 K was measured.

## Experiment

### *Sample preparation*

A sample of polycrystalline Mg-doped  $\alpha$ -alumina was prepared by a solid-state reaction method. The reagent-grade  $\text{Al}_2\text{O}_3$  (99.99 %) and  $\text{MgAl}_2\text{O}_4$  (99.9 %) powders were weighed to form the composition  $\text{Al}_{2-x}\text{Mg}_x\text{O}_{3-\delta}$  ( $x=0.001, 0.01$ ). These powders were mixed using a mortar made of  $\alpha$ -alumina. The powder mixture was then pressed into a pellet at 1 t/cm<sup>2</sup> and then sintered at 1873 K for 10 h in air. The X-ray powder diffraction analysis of the crushed sample powder

gave a well-defined mixed pattern of corundum and spinel. It was found that all samples contained small precipitates of  $\text{MgAl}_2\text{O}_4$ . The sintered sample was annealed under  $x\%\text{H}_2\text{O}-y\%\text{O}_2\text{-Ar}$  ( $x=1-10$ ,  $y=1-99$ ) at 1873 K for 18-240 h. The pressure of the water vapor was controlled by using an  $\text{O}_2\text{-Ar}$  mixture containing specific amounts of water vapor to equilibrium in a thermostatic bath that was held at the appropriate temperature.

#### *Measurement of electrical conductivities*

The electrical conductivity of the sample was measured by a two-probe ac method under equilibrium conditions with the gas mixtures of  $\text{H}_2\text{O}-\text{H}_2\text{-Ar}$ ,  $\text{D}_2\text{O}-\text{D}_2\text{-Ar}$  or  $\text{H}_2\text{O}-\text{O}_2\text{-Ar}$  in the temperature range of 1073-1473 K. The disk-shaped sample is placed so as not to contact any materials except for the platinum lead [11]. Porous platinum electrodes were prepared on both surfaces of the sample disk by joining with paste and then sintering in air. The complex impedance of the samples was measured using an impedance analyzer (NF LCZ2345 and HP 4192A).

## **Results**

#### *$\text{H}^+/\text{D}^+$ isotope effect on the electrical conductivity*

Fig.1 shows the electrical conductivity of the untreated sample. The  $p_{\text{H}_2}$  in this paper represents the activity of hydrogen with reference to one bar of hydrogen gas in the pure state. The  $\text{H}^+/\text{D}^+$  isotope effect on the conductivity was observed under  $1\%\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ )- $3\%\text{H}_2$  (or  $\text{D}_2$ )-Ar at 1273 K. The obtained value of the ratio of conductivities was nearly equal to the value theoretically estimated based on the hopping of a proton and a deuteron among the equivalent sites located between two oxide ions. It was then found that the dominant charge carrier of the Mg-doped polycrystalline  $\alpha$ -alumina is a proton. The chemical diffusion coefficient of the  $\text{H}^+/\text{D}^+$  diffusion pair was determined by the relaxation time of the change in the ohmic resistance when the measuring atmosphere was changed from  $1\%\text{H}_2\text{O}-3\%\text{H}_2\text{-Ar}$  to  $1\%\text{D}_2\text{O}-3\%\text{D}_2\text{-Ar}$ . The normalized change in the ohmic resistance of the thin planar sheet with the thickness  $2l$  can be represented by [11]

$$\frac{R(t) - R(0)}{R(\infty) - R(0)} = \frac{1}{2l} \int_{-l}^l \frac{1}{\left(1 - \frac{R(\infty)}{R(0)}\right) + \frac{R(\infty)}{R(0)} \frac{C_0}{C(x,t)}} dx \quad (1)$$

where  $R(0)$  and  $R(\infty)$  are the resistances of the sample equilibrated with 1% $\text{H}_2\text{O}$ -3% $\text{H}_2$ -Ar and 1% $\text{D}_2\text{O}$ -3% $\text{D}_2$ -Ar, respectively.  $R(t)$  is the ohmic resistance of the sample at time  $t$ .  $C_0$  is the initial concentration of a proton and  $C(x, t)$  is the concentration of a deuteron at time  $t$  and position  $x$ . The deuteron concentration in this case is represented by the following equation [19]

$$\frac{C(x,t)}{C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\frac{\tilde{D}(2n+1)^2 \pi^2 t}{4l^2}\right) \cos \frac{(2n+1)\pi x}{2l} \quad (2)$$

where  $\tilde{D}$  is the chemical diffusion coefficient of the  $\text{H}^+/\text{D}^+$  diffusion pair. With the chemical diffusion coefficient as the parameter,  $R(t)$  calculated by Eqs. (1) and (2) was fitted to the measurement value. The best fitting curve is shown by the solid line in Fig. 1. The chemical diffusion coefficient thus determined was  $1.7 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$  at 1273 K.

For the untreated specimen, the electrical conductivity under equilibrium conditions with 1% $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ )-1% $\text{H}_2$  (or  $\text{D}_2$ )-Ar were measured. The results were shown as a function of the temperature in Fig. 2. In this measurement, the measurement temperature was gradually raised from 1073 K. A decrease in the conductivity was observed at 1473 K. The change of the conductivity at 1473 K from the higher to the lower value was taken 800 hours. The  $\text{H}^+/\text{D}^+$  isotope effect on the conductivity was also observed in the state exhibiting the lower value. The activation energy of the conductivity of the sample after exhibiting the lower value was determined from the temperature dependence. The value was 1.0 eV and almost the same as that determined for the untreated specimen in the low temperature range.

#### *Atmosphere dependence of the electrical conductivity*

Fig. 3 shows the hydrogen activity dependence of the electrical conductivity at 1273 K. The measurement sample was annealed under 1% $\text{H}_2\text{O}$ -99% $\text{O}_2$  at 1873 K for 240 h. As shown in the figure, the electrical conductivity was independent of the hydrogen activity in the hydrogen atmosphere ( $p_{\text{H}_2} = 0.01$ -0.99). On the contrary, the electrical conductivity was proportional to the

-1/2 power of the hydrogen activity in the oxidizing atmosphere ( $p_{H_2} = 10^{-8}$ - $10^{-10}$ ). Fig. 4 shows the water vapor activity dependence of the electrical conductivity. As shown in figure, the dependence of the electrical conductivity was not observed when the oxygen activity or the hydrogen activity was fixed when in the hydrogen atmosphere ( $p_{H_2} = 0.01$ - $0.99$ ). On the other hand, the dependence was only observed when the oxygen activity ( $p_{O_2} = 0.01$ ) was fixed in the oxidizing atmosphere.

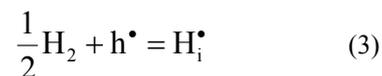
#### *Annealing effect on the electrical conductivity*

Fig. 5 shows the relation between the activity of oxygen in the annealing atmosphere at 1873 K and the conductivity measured at 1273 K. As shown in the figure, the electrical conductivity measured at 1273 K increased with the increase in the activity of oxygen in the annealing atmosphere. The relation between the activity of the water vapor in the annealing atmosphere at 1873 K and the conductivity measured at 1273 K is shown in Fig. 6. The electrical conductivity measured at 1273 K was found to increase with the increase in the activity of water vapor in the annealing atmosphere.

## **Discussion**

#### *Defect structure of Mg doped $\alpha$ -alumina*

In our previous studies, the defect structure of a single crystal of  $\alpha$ -alumina doped with a bivalent cation was examined [10-13]. According to these works, the equilibrium reaction between the defects in the crystal and the ambient atmosphere is represented as follows:



As the defect concentration is low, Henry's law is applicable. The following relation applies when the equilibrium state is obtained.

$$K = \frac{[H_i^\bullet]}{[h^\bullet] p_{H_2}^{1/2}} \quad (4)$$

where  $K$  is the equilibrium constant for Eq. (3) and  $[i]$  is the concentration of species  $i$  represented by moles in one mole of  $Al_2O_3$ .

The electroneutrality condition is expressed as follows:

$$[M'_{Al}] = [H_i^\bullet] + [h^\bullet] \quad (5)$$

where  $M'_{Al}$  is a dissolved bivalent cation substituted on an aluminum site. Based on Eqs. (4) and (5), the conductivity of the proton and positive hole are expressed as follows:

$$\sigma_{H_i^\bullet} = F m_{H_i^\bullet} \frac{[M'_{Al}] K p_{H_2}^{1/2}}{1 + K p_{H_2}^{1/2}} \frac{1}{V_{Al_2O_3}} \quad (6)$$

$$\sigma_{h^\bullet} = F m_{h^\bullet} \frac{[M'_{Al}]}{1 + K p_{H_2}^{1/2}} \frac{1}{V_{Al_2O_3}} \quad (7)$$

where  $m_i$  and  $V_{Al_2O_3}$  are the drift mobility of species  $i$  and the molar volume of  $\alpha$ -alumina. As shown in Figs. 3 and 4, the electrical conductivity of the Mg-doped polycrystalline  $\alpha$ -alumina was only dependent on the hydrogen activity. This result agrees with the electrical conductivity of a single crystal. The self-diffusion coefficient of the proton can be estimated from the chemical diffusion coefficient of the  $H^+/D^+$  diffusion pairs [20]. The drift mobility of the proton can be evaluated from the self-diffusion coefficient using the Nernst-Einstein relation. The evaluated mobility of proton was  $1.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at 1273 K for the Mg-doped polycrystalline  $\alpha$ -alumina. The equilibrium constant of Eq. (3), which can be regarded to be independent of the kind of species of the divalent dopant, was reported in a previous study as follows[11]:

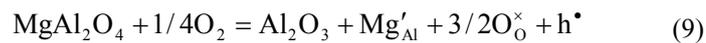
$$\ln K = \frac{1.6 \times 10^5 \text{ J mol}^{-1}}{RT} - \frac{40 \text{ J mol}^{-1} \text{ K}^{-1}}{R} \quad (8)$$

By setting the mobility of the positive hole and the concentration of magnesium ion as fitting parameters, the calculated total conductivities based on Eqs. (6), (7) and (8) using the mobility data of the proton were fitted to the measured values as shown in Fig. 3. The calculated value, which was indicated by a solid line, was in agreement with the measured value. The value of the mobility of the positive hole and the concentration of magnesium ions used as fitting parameters were  $1.3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and  $5.5 \times 10^{-7} \text{ mol cm}^{-3}$ , respectively.

#### *Decrease in electrical conductivity and annealing effect*

As shown in Fig. 2, a decrease in the electrical conductivity was observed at 1473 K. Judging from the isotope effect, the proton is the dominant charge carrier under this condition. According to Eq. (6), it is postulated that the decrease in the protonic conductivity is attributed to the decrease in the concentration of the magnesium ion. Therefore, it is considered that the peak amount of magnesium ion attained at the sintering temperature in  $\alpha$ -alumina has been frozen in a nonequilibrium state at less than 1473 K, but it reaches to the equilibrium value in a possible time above 1473 K.

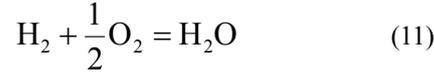
In this study, the annealing effect at 1873 K on the electrical conductivity was examined. As shown in Figs. (5) and (6), the electrical conductivity measured at 1273 K increased with the increase in the activity of oxygen and water vapor in the annealing atmosphere at 1873 K. The annealing sample contains precipitated  $\text{MgAl}_2\text{O}_4$  as the second phase. Norby and Kofstad reported that the positive holes in commercially supplied alumina are compensated with  $\text{Fe}'_{\text{Al}}$  and  $\text{Mg}'_{\text{Al}}$  in equilibrium with the precipitates of  $\text{FeAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  at 1673 K [14]. In this annealing condition, the equilibrium reaction between the precipitated spinel and  $\alpha$ -alumina is represented as follows:



The equilibrium constant of eq. (9) can be expressed as follows:

$$K' = \frac{[\text{Mg}'_{\text{Al}}][\text{h}\cdot]}{p_{\text{O}_2}^{1/4}} \quad (10)$$

The following equilibrium now holds.



$$K_{\text{W}} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} \quad (12)$$

where  $K_{\text{W}}$  denotes the equilibrium constant of Eq. (11). Based on Eqs. (4), (5), (10) and (12), the concentration of magnesium ion at 1873 K, which is annealing temperature, is represented as follows:

$$[\text{Mg}'_{\text{Al}}] = \left\{ K'_{1873\text{K}} \left( p_{\text{O}_2, 1873\text{K}}^{1/4} + \frac{K_{1873\text{K}}}{K_{\text{W}1873\text{K}}^{1/2}} p_{\text{H}_2\text{O}, 1873\text{K}}^{1/2} \right) \right\}^{1/2} \quad (13)$$

According to Eq. (13), the concentration of magnesium ions in  $\alpha$ -alumina increases with the increase in the oxygen and water vapor activities under the annealing conditions. This enhanced amount of magnesium ions is frozen in the nonequilibrium state to 1273 K. If the reaction about the hydrogen incorporation represented by Eqs.(3) attains the equilibrium at the measuring temperature, the protonic conductivity at 1273 K is represented from Eqs. (6) and (13), as follows:

$$\sigma_{\text{H}^+, 1273\text{K}} = Fm_{\text{H}^+, 1273\text{K}} \left\{ K'_{1873\text{K}} \left( p_{\text{O}_2, 1873\text{K}}^{1/4} + \frac{K_{1873\text{K}}}{K_{\text{W}1873\text{K}}^{1/2}} p_{\text{H}_2\text{O}, 1873\text{K}}^{1/2} \right) \right\}^{1/2} \frac{K_{1273\text{K}} p_{\text{H}_2, 1273\text{K}}^{1/2}}{1 + K_{1273\text{K}} p_{\text{H}_2, 1273\text{K}}^{1/2}} \frac{1}{V_{\text{Al}_2\text{O}_3}} \quad (14)$$

By setting the equilibrium constant of Eq. (10),  $K'_{1873\text{K}}$ , as a fitting parameter, the calculated protonic conductivities based on Eqs. (8) and (14) were fitted to the measured value as shown in Figs. (5) and (6). The fitted curves are denoted by the broken line. The dependencies of the electrical conductivity can be successfully fitted by this model as shown in the figures. The

equilibrium constant of Eq. (9) at 1873 K,  $K'_{1873\text{K}}$ , thus determined was to be  $1.2 \times 10^{-5}$ . The oxygen activity dependence of the defects concentration was estimated from this equilibrium constant. The result is shown in Fig. 7. As shown in figure, the concentration of magnesium ion increased with the increase of oxygen activity in an annealing atmosphere.

The results of this study show that Mg doped alumina annealed in the high oxygen activity exhibits the best performance as proton conductor.

### **Summary**

In order to optimize the manufacturing conditions of sintered  $\alpha$ -alumina as the electrolyte of a galvanic-type hydrogen sensor, the electrical conductivity of Mg-doped polycrystalline  $\alpha$ -alumina annealed at various conditions of the surrounding atmosphere was measured. The electrical conductivity measured at 1273 K increased with an increase in the activity of oxygen and water vapor in the annealing atmosphere at 1873 K. This phenomenon is attributed to the annealing effect on the magnesium ion concentration determined by the partition between the bulk and a small amount of the second phase. The best manufacturing condition of this material as a proton conducting solid electrolyte was found to keep the activities of oxygen and water vapor in sintering atmosphere as high as possible.

### **Acknowledgements**

This study was partly supported by a Grant-in-Aid for Science Research (19206081) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and a Grant for SENTAN from JST.

## References

- [1] Rochow E G 1938 *J. appl. Phys.*, **9** 664
- [2] Wachtman Jr. J B and Maxwell L H 1954 *J. Am. Cer. Soc.*, **37** 291
- [3] Harrop P J and Creamer R H, 1963 *Br. J. Appl. Phys.*, **14** 335
- [4] Champion J A 1964 *Br. J. Appl. Phys.*, **15** 633
- [5] Dasgupta S 1966 *Br. J. Appl. Phys.*, **17** 267
- [6] ÖZkan O T and Moulson A J 1970 *J. Physics D: Applied Physics*, **3** 983
- [7] Kitazawa K and Coble R L 1974 *J. Am. Cer. Soc.*, **57** 245
- [8] El-Aiat M M and Kröger F A 1982 *J. Appl. Phys.*, **53** 3658
- [9] Fukatsu N, Kurita N, Oka Y and Yamamoto S 2003 *Solid State Ionics*, **162-163** 147
- [10] Okuyama Y, Kurita N and Fukatsu N 2006 *Advanced Materials Research* **11-12** 145
- [11] Okuyama Y, Kurita N and Fukatsu N, 2009 *Solid State Ionics* **180** 175
- [12] Okuyama Y, Kurita N and Fukatsu N, 2009 *J. Min. Mater. Process. Inst. Jpn.* **125** 389
- [13] Okuyama Y, Kurita N, and Fukatsu N, 2010 *Solid State Ionics* **181** 142
- [14] Norby T and Kofstad P 1988 *High Temp. High Press.* **20** 345.
- [15] Kurita N, Fukatsu N, Miyamoto N, Takada M, Hara J, Kato M and Ohashi T 2003 *Solid State Ionics* **162-163** 135
- [16] Okuyama Y, Kurita N, Yamada A, Takami H, Oshima T, Katahira K and Fukatsu N 2009 *Electrochimica Acta* **55** 470
- [17] Kurita N, Ootake K and Fukatsu N 2011 *J. Electrochem. Soc.* **158** B667
- [18] Iwahara H, Esaka T, Uchida H and Maeda N 1981 *Solid State Ionics* **3/4** 359
- [19] Crank J 1975 *The Mathematics of Diffusion*, 2<sup>nd</sup> ed. Clarendon Press, Oxford 47
- [20] Waser R 1986 *Ber. Bunsenges. Phys. Chem.* **90** 1223.

Figure caption

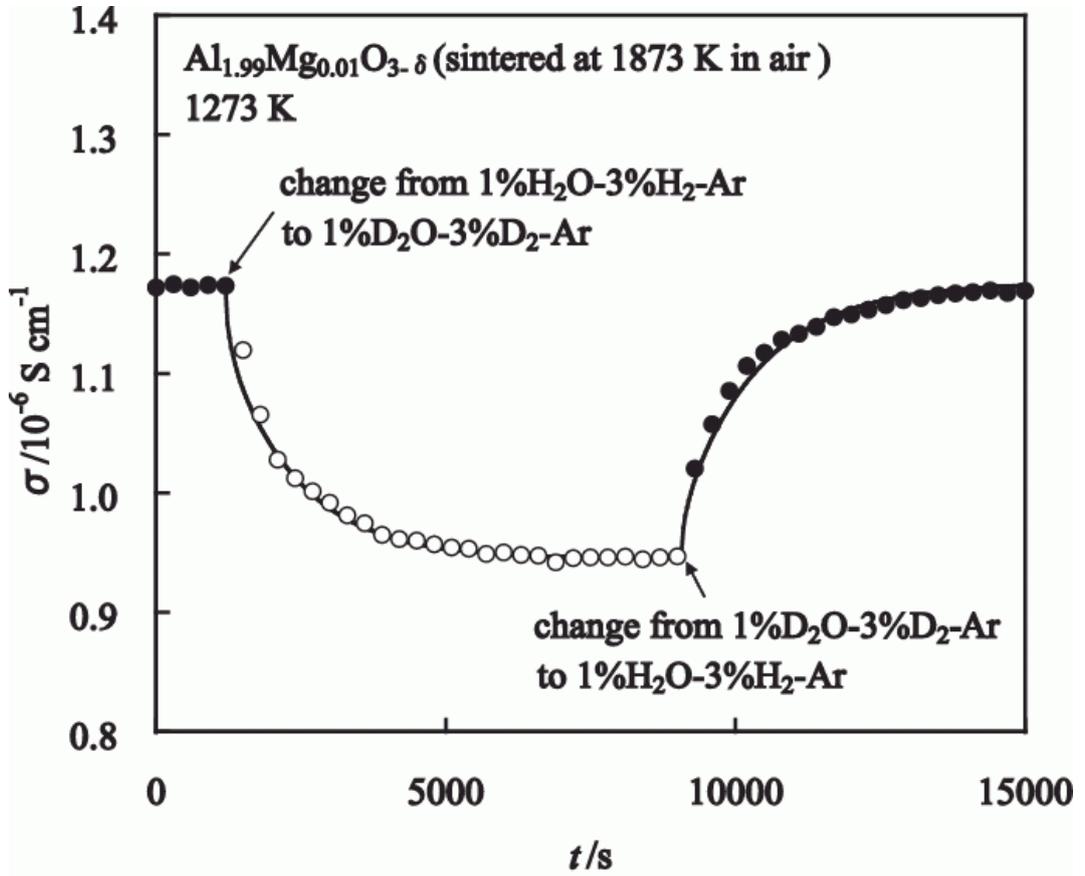


Fig. 1  $\text{H}^+/\text{D}^+$  isotope effect on electrical conductivity of Mg-doped  $\alpha$ -alumina.

Fig. 1  $\text{H}^+/\text{D}^+$  isotope effect on electrical conductivity of Mg-doped  $\alpha$ -alumina.

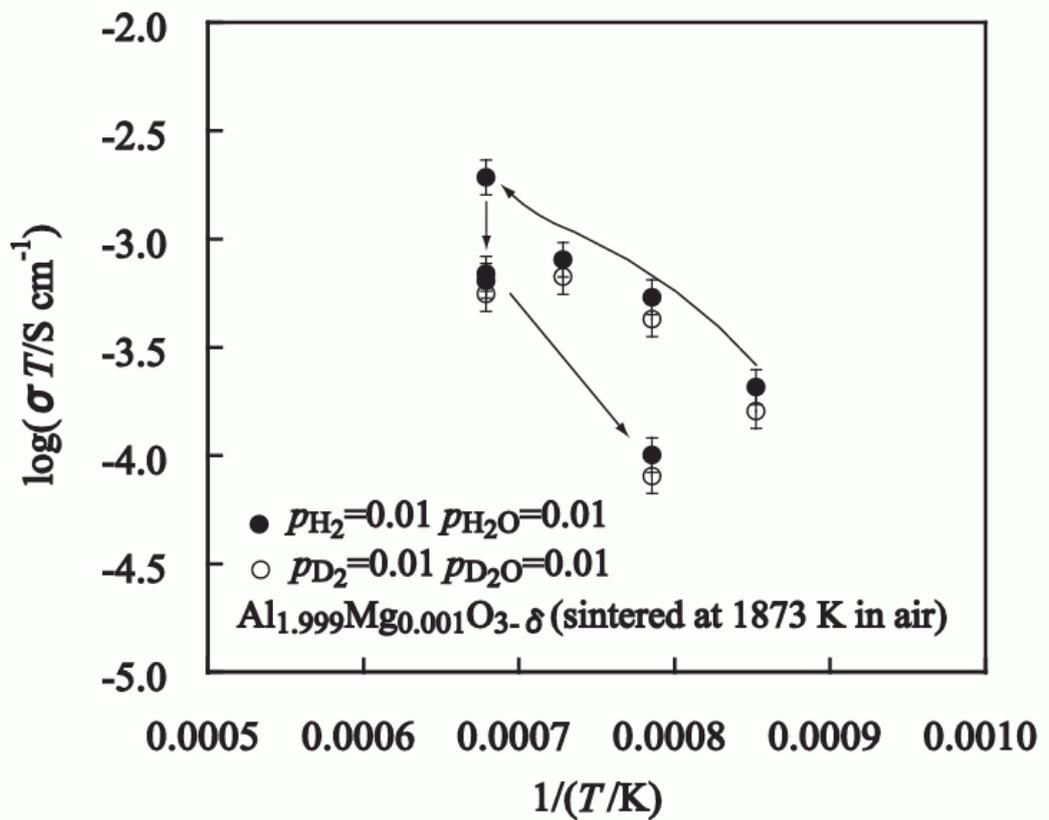
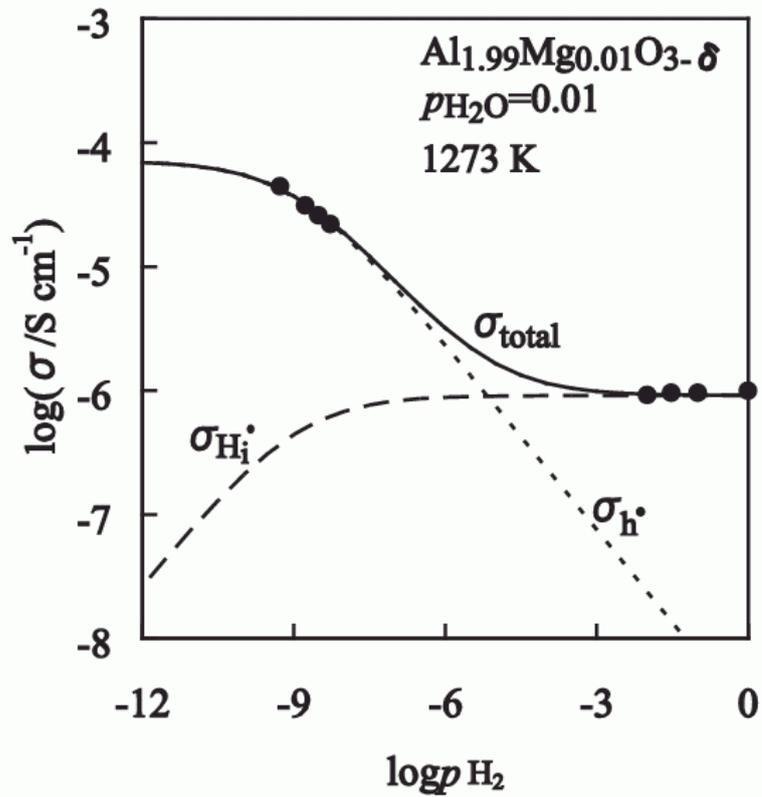


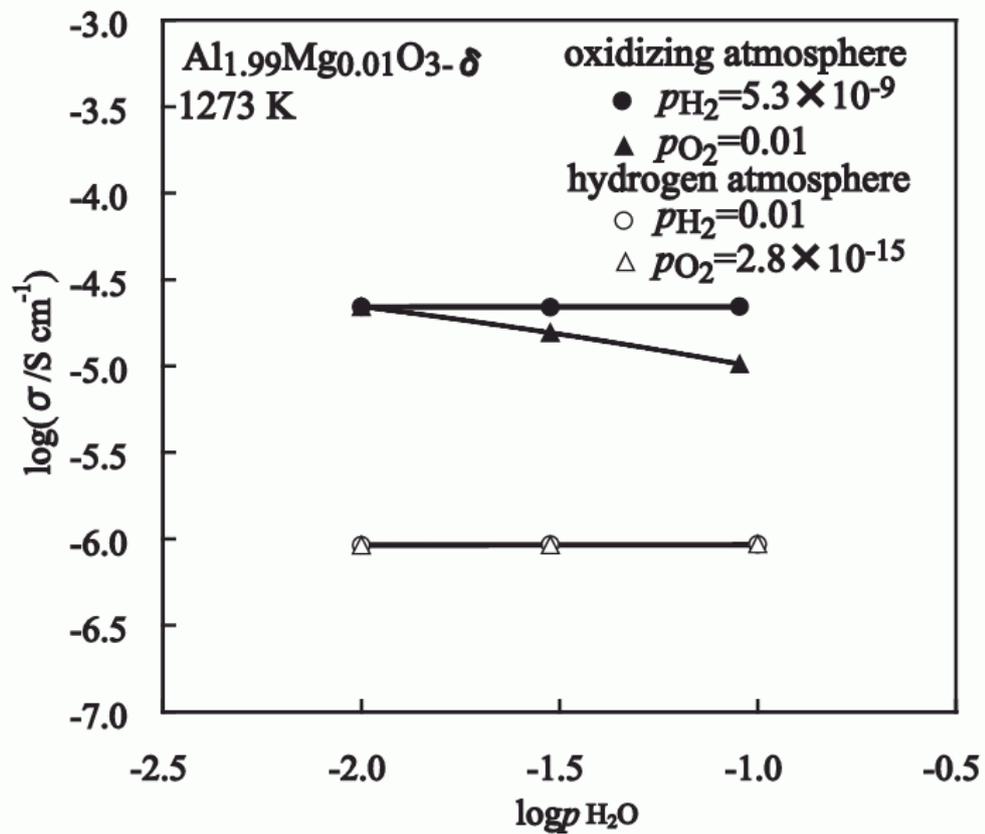
Fig. 2 Arrhenius-type plots of electrical conductivity for Mg-doped  $\alpha$ -alumina.

Fig. 2 Arrhenius-type plots of electrical conductivity for Mg-doped  $\alpha$ -alumina.



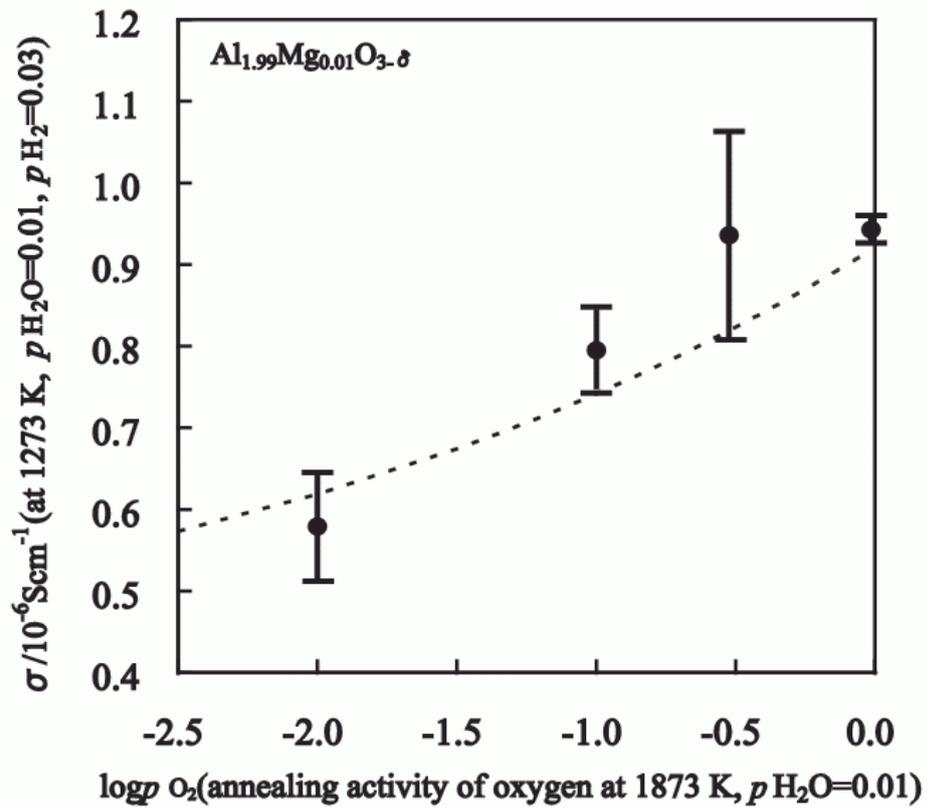
**Fig. 3 Effect of hydrogen activity on the electrical conductivity of Mg-doped polycrystalline  $\alpha$ -alumina.**

Fig. 3 Effect of hydrogen activity on the electrical conductivity of Mg-doped polycrystalline  $\alpha$ -alumina.



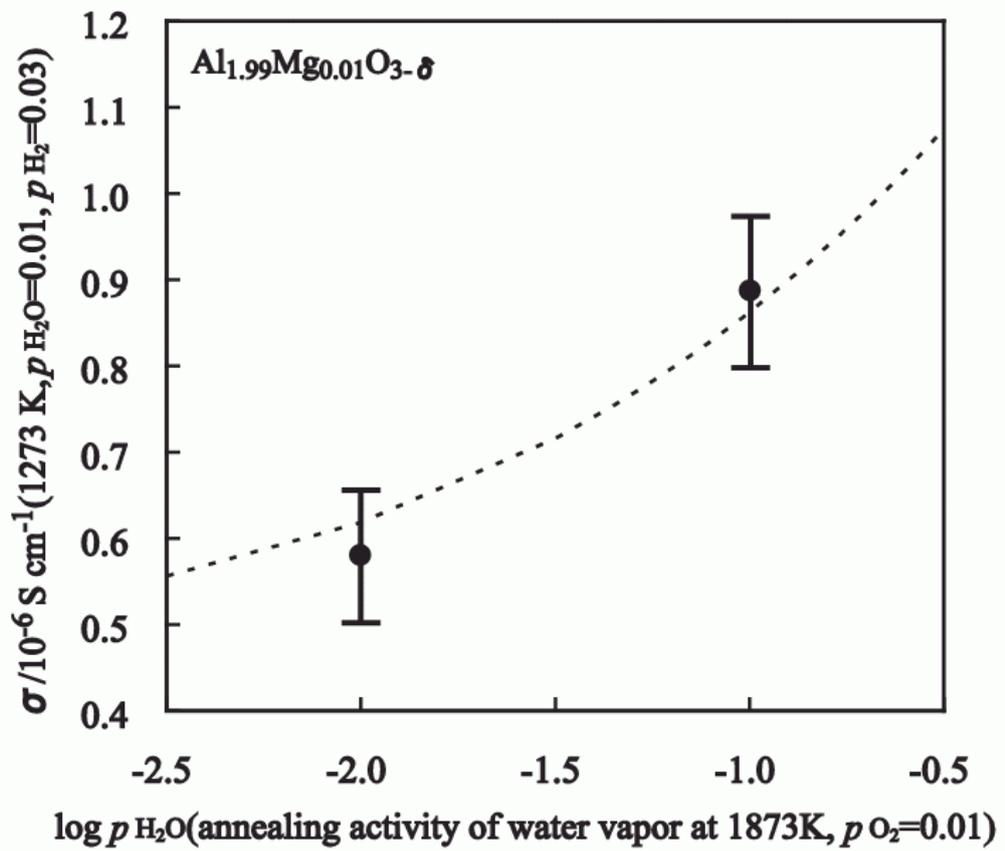
**Fig. 4 Effect of water vapor activity on the electrical conductivity of Mg-doped polycrystalline  $\alpha$ -alumina.**

Fig. 4 Effect of water vapor activity on the electrical conductivity of Mg-doped polycrystalline  $\alpha$ -alumina.



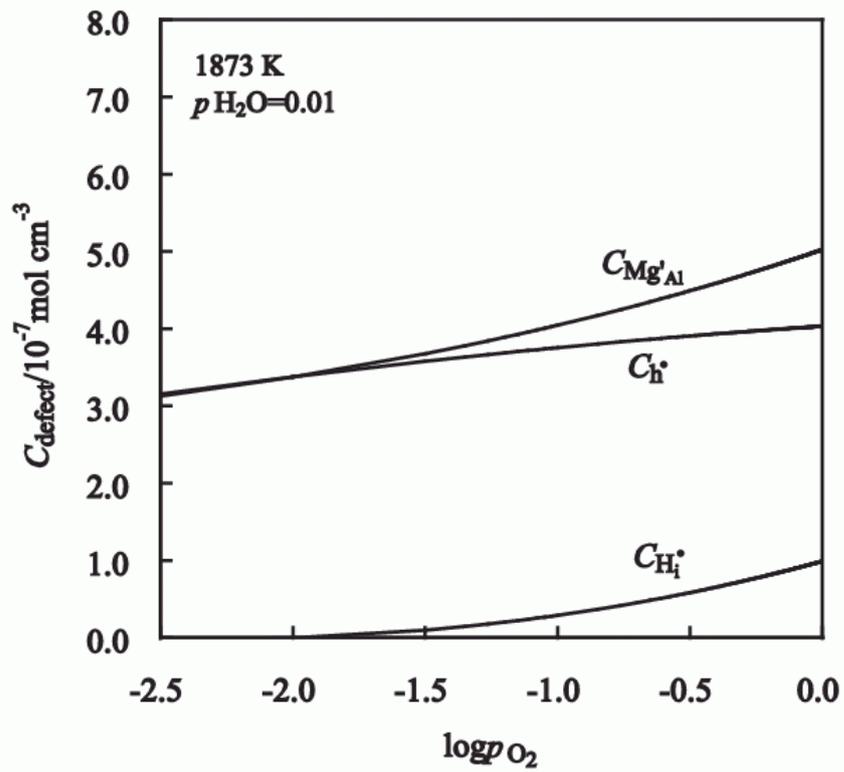
**Fig. 5 The effect of the oxygen activity in an annealing atmosphere on the electrical conductivity measured at 1273 K.**

Fig. 5 The effect of the oxygen activity in an annealing atmosphere on the electrical conductivity measured at 1273 K.



**Fig. 6** The effect of the annealing water vapor activity on the electrical conductivity measured at 1273 K.

Fig. 6 The effect of the annealing water vapor activity on the electrical conductivity measured at 1273 K.



**Fig. 7** The effect of oxygen activity in an annealing atmosphere on the defect concentration.

Fig. 7 The effect of the oxygen activity in an annealing atmosphere on the defect concentration.